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(71) Applicant: **MALLINCKRODT BAKER, Inc.**
Phillipsburg, New Jersey 08865 (US)

(72) Inventors:
• **Ilardi, Joseph M.**
Sparta, NJ 07871 (US)

• **Schwartzkopf, George,**
Franklin Township, NJ 07882 (US)
• **Dalley, Gary G.**
Easton, PA 18042 (US)

(74) Representative: **VOSSIUS & PARTNER**
Siebertstrasse 4
81675 München (DE)

(54) **pH Adjusted nonionic surfactant containing alkaline cleaner composition for cleaning microelectronics substrates**

(57) Aqueous alkaline cleaning solutions for cleaning microelectronic substrates and maintaining substrate surface smoothness comprise a metal ion free base, a nonionic surfactant and a component to reduce or control the pH of the cleaning solution to a pH within the range of from about pH 8 to about pH 10.

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EUROPEAN SEARCH REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-4 612 058 (GEKE JUERGEN ET AL) 16 September 1986 * column 2, line 6 - column 3, line 28; claims 1-7; examples 6-9 *	1,2,5,6	C11D3/30 C11D3/20 C11D1/74 C11D1/72 C11D1/66
A	US-A-3 886 099 (HALL ROBERT M) 27 May 1975 * whole document *	1-16	
A,D	US-A-4 339 340 (MURAOKA HISASHI ET AL) 13 July 1982 * column 6, line 38 - column 10, line 48; claims 1-34 *	3,4, 8-11,15, 16	
A,D	US-A-4 239 661 (ASANO MASAFUMI ET AL) 16 December 1980 * column 6, line 38 - column 10, line 45; claims 1-32 *	3,4, 8-11,15, 16	
A	WO-A-93 14884 (SACHEM INC) 5 August 1993 * page 5, line 12 - page 12, line 10; claims 1-19 *	3,4,8,9, 15,16	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C11D
A	GB-A-1 573 208 (TOKYO SHIBAURA ELECTRIC LTD) 20 August 1980 * whole document *	3,4,8,9, 15,16	
A	EP-A-0 578 507 (EKC TECHNOLOGY INC) 12 January 1994 * page 6, line 29 - page 8, line 14; claims 1-19 *	5,8,9, 15,16	
A	US-A-4 833 067 (TANAKA HATSUYUKI ET AL) 23 May 1989 * column 3, line 51 - column 4, line 59; claim 1 *	6,7,15, 16	
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 19 November 1996	Examiner Ainscow, J
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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removed this residual ash without damaging any silicon or metal features that were present.

	pH Reducing Component	pH
5	Ammonium acetate	9.3-10.0
	Ammonium acetate, ammonium hydroxide	9-10
	Acetic acid, ammonium hydroxide	9.5-10
10	Acetic acid, 1-amino-2-propanol	9.5-10
	Acetic acid, hydrogen peroxide	9.3
	Ammonium acetate, hydrogen peroxide	9.5
	Ammonium acetate, nitric acid	9.5
15	Ammonium nitrate	8.9-10.0
	Ammonium chloride, ammonium acetate, hydrogen peroxide	9.6-10.0
	Ammonium chloride, ammonium acetate, ammonium periodate	9-10
20	Ammonium chloride, ammonium acetate, ammonium nitrate	9.4-10.0
	Ammonium chloride, ammonium acetate, ammonium persulfate	9-10

Photoresist ash residues were successfully removed. The bath was analyzed for silicon content after use giving <0.2 ppm of dissolved Si demonstrating that the desired cleaning was achieved without etching exposed silicon or silicon dioxide circuit elements.

EXAMPLE 7

This example demonstrates the metal removal capabilities of a cleaner formulation for the removal of aluminum, copper, and iron from metal-contaminated silicon wafers. Cleaner Formulation A was prepared by dissolving ethylenediaminetetraacetic acid (EDTA), ammonium acetate, tetramethyl ammonium hydroxide, and 3,5-dimethylhexyne-3-ol in deionized water. Cleaner Formulation B was similarly prepared substituting nitrilotriacetic acid (NTA) for the EDTA. Both formulations exhibited a pH of approximately 10. Metal-contaminated wafers were cleaned in these solutions for 10 minutes at 70 °C. The wafers were removed from the cleaner, rinsed in deionized water, and dried. The remaining amount of wafer metal contamination was measured by washing the wafers with dilute hydrochloric acid which was then analyzed for aluminum, copper, and iron. The observed results were as follows.

	Cleaning Formulation	Aluminum (micrograms/wafer)	Copper (micrograms/wafer)	Iron (micrograms/wafers)
40	none	1	1	0.9
	Formulation A	0.1	<0.01	0.2
45	Formulation B	0.06	<0.01	0.1

EXAMPLE 8

In another embodiment of the present invention an aqueous alkaline cleaner (Formulation C) containing tetramethyl ammoniumhydroxide (0.5%), EDTA (0.1%), ammonium chloride (0.3%), ammonium acetate (0.3%), hydrogen peroxide (1.0%), and 3,5-dimethylhexyne-3-ol (0.1%) was directly compared to a conventional SC-1 cleaner containing, by volume, one part concentrated ammonium hydroxide, one part 30% hydrogen peroxide, and five parts of deionized water. Both cleaning solutions were purposely contaminated with 5 micrograms/liter each of aluminum, iron, and nickel, and 10 micrograms/liter of copper introduced as nitrate salts. Silicon wafers were cleaned in these solutions for 10 minutes at 70 °C after which they were rinsed in deionized water, and dried. Residual metal contamination on the wafers was then

measured using hydrogen fluoride vapor phase decomposition of the native oxide layer of the silicon wafer followed by scanning the wafer surface with a small volume of water. This water was removed and analyzed by inductively coupled plasma analysis with mass spectral detection giving the following results.

Cleaning Formulation	x 10 ¹⁰ atoms/cm ²			
	Aluminum	Copper	Nickel	Iron
none (untreated wafer)	42	<6	21	72
SC-1	2,800	<15	5	743
Formulation C	52	<6	<2	35

These data clearly show the superior cleaning ability of Formulation C versus that of a conventional cleaner for metal removal from silicon wafer surfaces.

EXAMPLE 9

Silicon wafers were cleaned as in Example 8 and an Atomic Force Microscope (AFM) was used to examine the surfaces for roughness before and after cleaning. Roughness is reported in this example as "mean roughness" (R_a) which is defined as the mean value of the surface relative to the center plane and is calculated using:

$$R_a = \frac{1}{L_y L_x} \int_0^{L_y} \int_0^{L_x} |f(x,y)| dx dy$$

where $f(x,y)$ is the surface relative to the center plane and L_x and L_y are the dimensions of the surface in two dimensions.

The untreated, polished wafer with its normal covering of native oxide has an R_a of 0.140 nanometers. When this surface is exposed to SC-1 the R_a value increases to 0.185 nanometers. However, exposure to Formulation C beneficially lowers this R_a value to 0.137 nanometers.

Sample	R_a (nanometers)
none (untreated wafer)	0.140
SC-1	0.185
Formulation C	0.137

EXAMPLE 10

Flamed 57 mm. quartz wafers were used which were stored in sealed quartz petri dishes to avoid organic contamination. These wafers were cleaned as in Example 8 and analyzed for organic contamination using plasma chromatography coupled with mass spectroscopy (PC/MS). This technique involves heating to volatilize any adhering organic materials. The volatilized molecules are ionized and separated into identifiable fractions by passing them through a potential gradient. The high sensitivity of PC/MS allows detection of one part of organic material in 10¹³ parts of matrix.

The untreated wafer was simply rinsed in deionized water for ten minutes at room temperature. The PC/MS spectrum for this untreated wafer had two ion mass peaks (293 and 337 mass units) which are due to the environmentally ubiquitous phthalate esters, common plasticisers used in laboratory equipment. A wafer cleaned as in Example 8 using SC-1, gave a PC/MS spectrum having six new ion mass peaks (300, 335, 371, 411, 436, 533 mass units) indicative of more organic contamination than the untreated control. A wafer cleaned as in Example 8 using a formulation containing TMAH (1%), EDTA (0.1%), ammonium chloride (0.3%), ammonium acetate (0.3%), hydrogen peroxide (7%) and 3,5-dimethylhexyne-3-ol (0.2%),

gave a PC/MS spectrum having three ion mass peaks (300, 337 and 372 mass units). This spectrum shows less organic contamination than that indicated for SC-1. Thus, this cleaner formulation of this invention reduces residual volatile organics on this wafer to less than the standard SC-1 treatment. This Example shows that negligible residue was left by the organic components of this formulation insuring that further IC
 5 processing can proceed without interference.

Claims

1. An alkaline cleaning solution for microelectronics substrates comprising an aqueous metal ion free
 10 base, a nonionic surfactant and an effective amount of a pH reducing chemical component to reduce or control the pH of the cleaning solution to a pH within the range of from about pH 8 to about pH 10.
2. An alkaline cleaning solution for microelectronics substrates according to Claim 1 comprising from
 15 about 0.1% to about 25% by weight of an aqueous metal ion free base selected from ammonium hydroxide, alkanolamines, guanidine, quaternary ammonium hydroxides and mixtures thereof, from about 0.01% to about 5% by weight of a nonionic surfactant selected from the group consisting of alkynol surfactants, fluorinated alkyl alkoxyates, fluorinated alkyl esters, fluorinated polyoxyethylene alkanols, aliphatic acid esters of polyhydric alcohols, polyoxyethylene monoalkyl ethers, polyox-
 20 yethylene diols, siloxane surfactants and alkylene glycol monoalkyl ethers and mixtures thereof and from about 0.1% to about 10% by weight of a pH reducing chemical component to reduce or control the pH of the cleaning solution to a pH within the range of from about pH 8 to about pH 10 and wherein the chemical component to reduce or control the pH of the cleaning solution is selected from the group consisting of acids, bases and their salts and buffer systems of weak organic acids and conjugate
 25 bases.
3. An alkaline cleaning solution according to any one of Claims 1 or 2 wherein the metal ion free base is selected from a tetraalkyl ammonium hydroxide wherein the alkyl group is an unsubstituted alkyl group or an alkyl group substituent with a hydroxy or alkoxy radical.
- 30 4. A cleaning solution according to any one of Claims 1 or 2 wherein the metal ion free base is selected from tetramethyl ammonium hydroxide, tetraethyl ammonium hydroxide and trimethyl-2-hydroxyethyl ammonium hydroxide.
5. A cleaning solution according to any one of Claims 1 or 2 wherein the metal ion free base is an
 35 alkanolamine or a guanidine compound.
6. A cleaning solution according to any one of Claims 1 to 5 wherein the nonionic surfactant is selected from the group consisting of alkynol surfactants, fluorinated polyoxyethylene alkanol surfactants, siloxane surfactants and alkylene glycol monoalkyl ether surfactants.
- 40 7. A cleaning solution according to Claim 6 wherein the nonionic surfactant is selected from the group consisting of 3,5-dimethylhexyne-3-ol, a fluorinated polyoxyethylene ethanol and butoxypropanol.
8. A cleaning solution according to any one of Claims 1 to 7 additionally comprising a metal chelating
 45 agent.
9. A cleaning solution according to Claim 8 wherein the metal chelating agent is ethylenediaminetetraacetic acid.
- 50 10. A cleaning solution according to any one of Claims 1 to 9 additionally comprising an oxidizing agent.
11. A cleaning solution according to Claim 10 wherein the oxidizing agent is selected from hydrogen peroxide, nitric acid and its salts, and the persulfate, periodate, perbromate, perchlorate, iodate, bromate or chlorate salts of ammonium.
- 55 12. A cleaning solution according to any one of Claims 1 to 11 wherein the chemical component to reduce the pH of the cleaning solution is selected from acetic acid, potassium biphthalate, a mixture of ammonium acetate with ammonium chloride, and a mixture of acetic acid with ammonia.

13. A cleaning solution according to any one of Claims **1**, **2** or **9** comprising water, tetramethyl ammonium hydroxide, 3,5-dimethylhexyne-3-ol, ammonium chloride and ammonium acetate.

14. A cleaning solution according to any one of Claims **1**, **2** or **9** comprising water, tetramethyl ammonium hydroxide, acetic acid, ammonia or an alkanolamine and 1-butoxy-2-propanol.

15. Use of a cleaning composition according to any one of Claims **1** to **14** for cleaning a microelectronics wafer substrate and maintaining wafer surface smoothness.

16. Use of a cleaning solution according to any one of Claims **1** to **14** for cleaning vias in a microelectronic wafer substrate.

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